2006 DOE Hydrogen Program Review

Hydrogen Storage by Spillover

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Project ID: ST28

Overview

Timeline

- Project start date: FY05
- Project end date: FY10
- Percent complete: 25%

Budget

- Total project funding
  - DOE share: $939,356
  - Contractor share: $280,000
- Funding received in FY05: $112,500
- Funding for FY06: $175,000

Barriers

- General
  - Weight & Volume
  - Rates (Refueling and discharge)
- Reversible Solid-State Material
  - Hydrogen Capacity & Reversibility
  - Lack of Understanding of H Physi- & Chemisorption

Partners

- Sample/adsorbed H Verification and Characterization

  NREL, NIST
- Plan industrial collaboration after the initial phase of study and sorbent optimization

Project Objectives

- To develop carbon-based hydrogen storage materials with capacities in excess of 6 wt% (and 45 g/L) at room temperature
  - To develop and optimize our new Bridge-Building Techniques for Spillover to enhance hydrogen storage
  - To obtain a mechanistic understanding for hydrogen spillover in nanostructured carbon-based materials for the purpose of hydrogen storage

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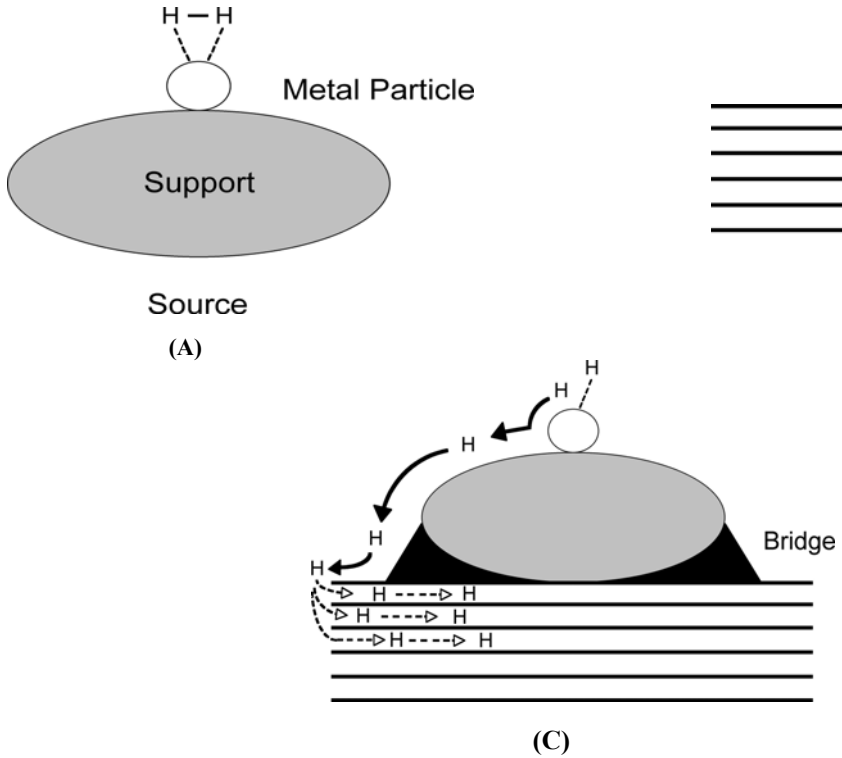
Approach

Strategy for storage by spillover: (A) Supported metal catalyst for H_2 dissociation; (B) Sorbent as receptor for H; (C) Building carbon bridges (by carbonization of a precursor) for spillover, resulting in a composite sorbent. (Yang et al., U.S. Patent application filed, 2005)



Theoretical Bases for the Spillover Approach

- H spillover (i.e., surface diffusion of H) is a well-known phenomenon since 1960's.
- H atoms can adsorb on the basal plane of graphite (i.e., saturated carbon site) (Chen and Yang, *Surf. Sci*., **216**, 481, **1989**)
- The bond energy for H on the basal-plane carbon depends on both density and distribution of H atoms, and can be as low as 27 kcal/mol (2 adjacent H). Dissociation and spillover was proposed for hydrogen storage. (Yang and Yang, *Carbon*, **40**, 437, **2002**)
- The bond energy of H on SWNT spans a wide range and also depends on both density and distribution of H (as well as tube size, etc.), and it can be as low as 8.9 kcal/mol (for 2 H adjacent on interior wall). (Yang, Lachawiec and Yang, J. *Phys. Chem. B.,* in press).
- *Thus, it is feasible to desorb hydrogen at room temperature.*

Approach

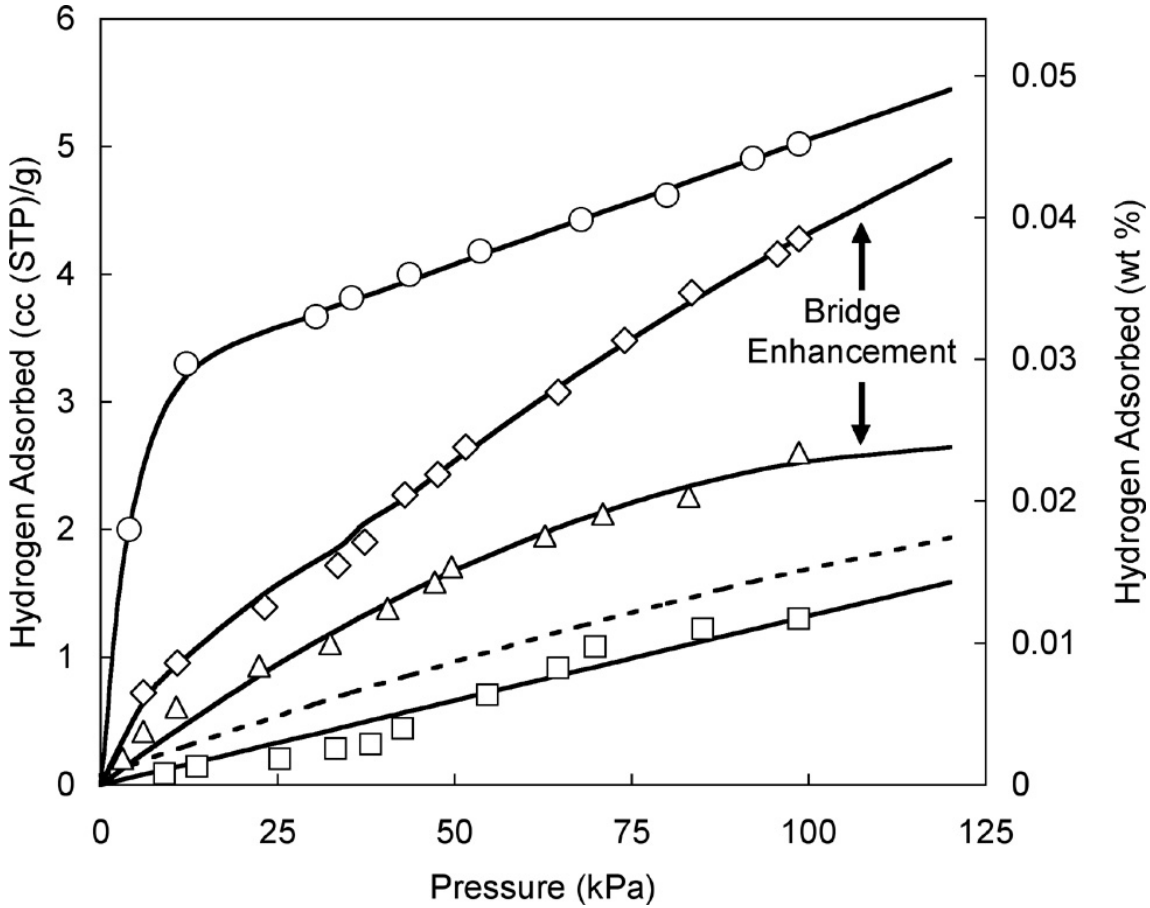
Strategy for bridge building (Yang et al., U.S. Patent application filed, 2005)**:**

- Select a proper precursor for carbon bridge (e.g., sugars, polymers)
- Melt mixture of precursor with catalyst and sorbent/receptor
- Follow an optimized temperature/gas environment treatment protocol (depending on the receptor and precursor as well as the catalyst) for optimized bridge-building
- Variables: metal catalyst, receptor, bridge precursor and bridge-building process.

Technical Accomplishments/ Progress/Results

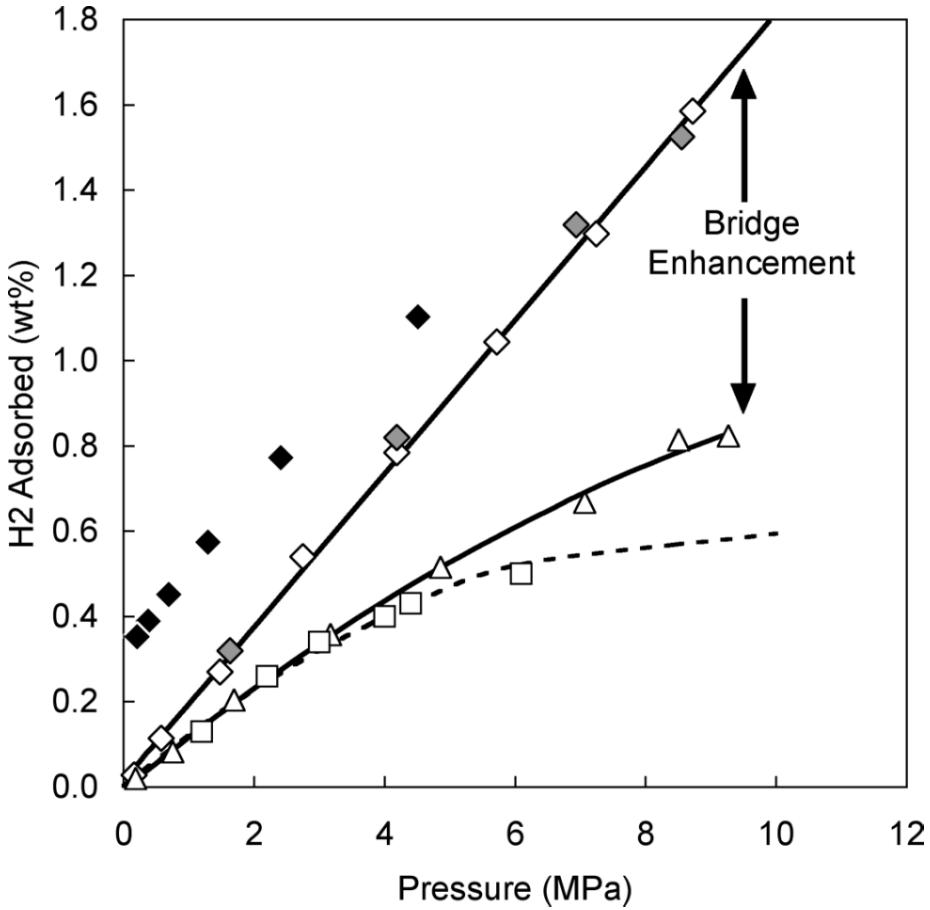
- Achieved 1.8 wt% hydrogen storage at 298K and 10 MPa by using AX-21 activated carbon and Pd/carbon catalyst with carbon bridges built for spillover.
- Achieved 1.8 wt% hydrogen storage at 298K and 10 MPa by using IRMOF-8 and Pt/carbon catalyst by spillover (without bridges).
- Preliminary results indicated the storage amount was near 4 wt% at 298K and 10 MPa for IRMOF-8 sample by using our bridge building technique.

Accomplishments/Progress/ Results Slides



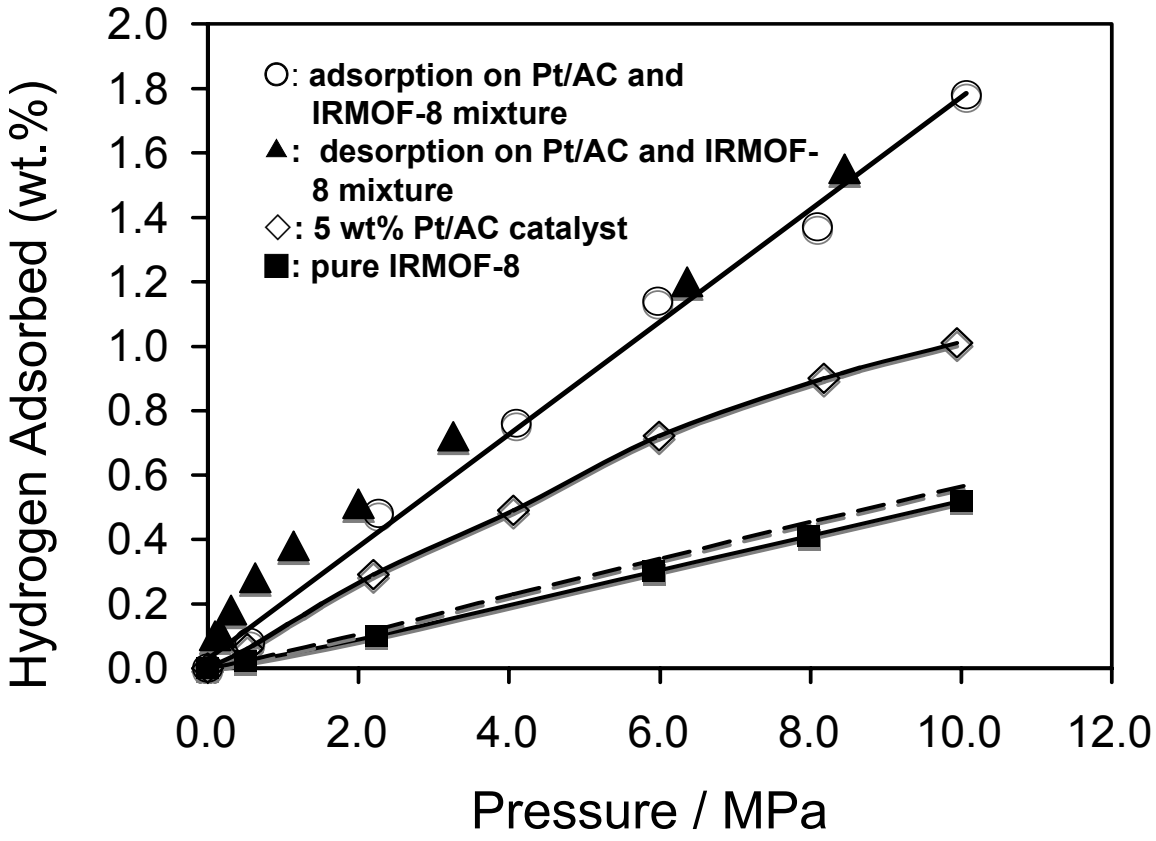
Low-pressure hydrogen isotherms at 298 K for AX-21 receptor. ○, 5 wt% Pd-C catalyst; ◇, AX-21/Pd-C/Carbon Bridge (8:1:1); △, AX-21/Pd-C physical mixture (9:1); □, AX-21; Dotted line is the sum of fractional contributions based on uptake of individual mixture components. (AX-21 is a high-surface area (~ 2600 m^2/g) activated carbon.)
(*Measured by Micromeritics instrument with maximum error of +/- 1%)*

Accomplishments Slides (con't)



High-pressure hydrogen isotherms at 298 K for AX-21 receptor.
△, AX-21/Pd-C physical mixture (9:1); □, AX-21.
◇, AX-21/Pd-C/Carbon Bridge (8:1:1) First Adsorption;
◆, AX-21/Pd-C/Carbon Bridge (8:1:1) Desorption;
◈, AX-21/Pd-C/Carbon Bridge (8:1:1) Second Adsorption.
Maximum error: +/- 10% (details of error analysis available)

Accomplishments Slides (con't)



High-pressure hydrogen isotherms at 298 K for IRMOF-8. Dotted line is prediction based on the weighted average of the mixture. Arrow indicates enhancement by spillover. (Isotherm for pure IRMOF-8 agrees with literature.)

Accomplishments Slides (con't)

Using the bridge-building technique, our current work indicates that the storage capacity for the sample of the best MOF, IRMOF-8, with Pt/AC catalyst and carbon bridges could reach ~ 4 wt% (40.8 g/L) at 298K and 10 MPa.

(To be published, 2006; U.S. Patent applied in 2005)

Future Work

- Test different receptors (sorbents) including MOFs and carbons (for sorbent candidates, see R. T. Yang, *Adsorbents: Fundamentals and Applications,* Wiley, New York, 2003).
- Test different catalysts and bridge-building precursors, as well as techniques for bridge building.
- Obtain basic understanding of the spillover process including equilibrium and kinetics.
- To achieve the DOE target of 4.5wt% (33.75 g/L) storage at 298K in FY 2006.
- To achieve the 5.5 wt% (41.25 g/L) DOE target at 298K in FY2007.
- To address issues on fueling rates and other DOE targets.

Summary

- Successfully developed the spillover technique for hydrogen storage by introducing a novel bridge building technique.
- Preliminary results indicate that the DOE material weight targets for storage could be achieved.

Summary Table

On-Board Hydrogen Storage System Targets

(*Data based on material only, not system value)

(** Based on a bulk density of 1.02 g/cm^3 for MOF-8)

Storage Parameter	Units	2010 System Target	FY06 Result* (Material)
Weight Storage Capacity	wt % H_2	6 wt%	4 wt%
Volumetric Storage Capacity	Kg H_2/L	45 g/L	40.8 g/L**
Desorption Temperature			298K

Maximum pressure used: 10 MPa (at 298K)

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Publications and Presentations

1. A. J. Lachawiec, Jr., G. S. Qi and R. T. Yang, "Hydrogen Storage in Nanostructured Carbons by Spillover: Bridge Building Enhancement," *Langmuir*, ***21***, 11418 (2005).
2. Y. W. Li and R. T. Yang, "Significant Enhancement of Hydrogen Storage Capacity in Metal-Organic Frameworks via Spillover," *J. Am. Chem. Soc.,* **128**, 726 (2006).
3. F. H. Yang, A. J. Lachawiec, Jr. and R. T. Yang, "Adsorption of Spillover Hydrogen Atoms on Single-Wall Carbon nanotubes," *J. Phys. Chem. B.*, In press.